Artifacts in Isothermal Crystallization Experiments of Polymers

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Experiments using differential scanning calorimeters (DSCs) are typically designed so as to minimize the effect of instrumental artifacts, for example using identical heating rates in dynamic experiments. In turn one hopes that instrument non-idealities will cancel one another out. With the advent of the PC, non-idealities in heat-flux instruments, which will have significantly more instrumental non-idealities can be, calculated and mathematically eliminated. Hence, it is not unreasonable to conclude that the careful experimenter can practically eliminate instrument non-idealities in most situations.

There are two sample non-idealities: low thermal conductivity and poor sample-pan contact. Non-idealities in dynamic experiments can be compensated for by running multiple experiments at multiple heat rates, through the use of modulating technology, or alternatively dispersing a powder sample in an inert heat-transfer fluid and measuring the thermal properties. Either approach is impossible for isothermal crystallization experiments; in the first case since one by definition wants to measure the heat rate, in the second case because wants an isothermal temperature and in the third case because melted droplets can coalesce in a liquid distorting the results. In this talk, after a brief description of the methods and uses of isothermal crystallization experiments to study polymer crystallization, the effect of artifacts in non-isothermal crystallization experiments in a power compensation DSC were quantitatively investigated. Our observations led us to conclude that poor-sample pan contact will occur occasionally, but one can easily identify those cases and simply discard that data. The limiting resistance to heat transfer is the thermal conductivity of the sample. We have proposed a method based on running different thickness samples which can be used to show the existence or absence of heat transfer effects but one cannot simply eliminate these effects due to extrapolation as can be done with rate experiments. The reason for this, we believe, is the existence of local hot-spots, and some admittedly non-conclusive experiments have been performed to show that the effect of these hot-spots can be mitigated by the addition of an inert solid filler.